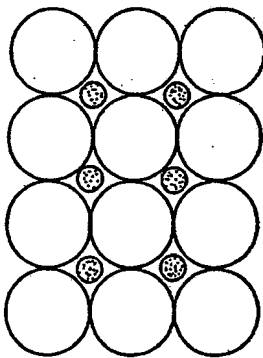


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(54) Title: HYPOCHLORITE DONOR/BROMIDE ION DONOR TABLETS WHICH ARE STABLE IN WATER○ ACL 90 GRANULES
⊗ NaBr GRANULES**(57) Abstract**

Disclosed is a water stable tablet for disinfecting recirculating water systems comprising chlorinated isocyanurate, sodium bromide and a stabilizer which regulates the rate at the chlorinated isocyanurate and the sodium bromide are dissolved or dispersed in flowing water. The stabilizer may be an active chlorine stabilizer compound that is compatible with chlorinated isocyanurates in the solid state, capable of binding active halogen (chlorine or bromine in the +1 valence state), and less soluble when fully chlorinated than in the less than fully chlorinated state.

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HYPOCHLORITE DONOR/BROMIDE ION DONOR
TABLETS WHICH ARE STABLE IN WATER

FIELD OF THE INVENTION

5 This invention relates to hypochlorite donor/bromide ion donor tablets for disinfecting recirculating water systems, and more particularly to tablets comprising chlorinated isocyanurates, sodium bromide, and a stabilizer which regulates the rate at which the
10 chlorinated isocyanurate and the sodium bromide are dissolved or dispersed in flowing water. The tablets according to the invention are stable in water, i.e., the tablets do not disintegrate into fines upon exposure to flowing water, but instead dissolve at relatively uniform
15 and commercially acceptable rates.

Tablets prepared according to the invention provide hypobromous acid, which functions as a bromine biocide or disinfectant in recirculating water systems such as cooling towers, swimming pools, spas, etc.

20 BACKGROUND OF THE INVENTION

A number of different compositions and methods that provide hypobromous acid for disinfecting recirculating water systems have been proposed.

British Pat. No. 1,196,870 discloses dry
25 disinfectant mixtures consisting essentially of the sodium salt of dichloroisocyanuric acid, trichloroisocyanuric acid, or a mixture thereof with an alkali metal bromide and a buffering mixture of sodium carbonate/bicarbonate and optionally including
30 phosphates, polyphosphates, and surface active agents.

U.S. Pat. No. 4,557,926, issued to Nelson et. al, discloses a tablet for disinfecting toilets comprising an alkali metal salt of dichlorocyanuric acid and either sodium bromide or potassium bromide.

35 U.S. Pat. No. 5,015,643, issued to Jones et. al, discloses solid disinfecting compositions comprising a mixture of 80% -99% by weight trichloro-s-triazinetriene and 1% - 20% by weight potassium bromide.

For recirculating water systems, it is preferable that a disinfectant composition be usable in biocide dispensing devices such as erosion feeders, skimmers, and floaters, in order to slowly release the disinfectant into the water system. The preferred disinfectant composition is a mixture of dry solid components that can be compressed into a tablet for use in these devices. Previous attempts to use disinfectant compositions comprising chlorinated isocyanurates and more than about 2 wt.% sodium bromide have not proved entirely satisfactory because the tablets have frequently failed to maintain their integrity as water is circulated through the dispensing device and instead disintegrated into small pieces or fines. Disintegration of the tablets leads to higher dissolution rates due to much higher exposed surface areas. As a result, the disinfectant is released too rapidly and at unpredictable rates.

As used herein, the term "hypochlorite ion donor" means any compound that will generate hypochlorite species when dissolved in water.

The term "chlorinated isocyanurate" means dichloroisocyanuric acid, trichloroisocyanuric acid, [mono(trichloro)-tetra(monopotassium dichloro)]-penta-s-triazinetriene, and [mono(trichloro)-mono(monopotassium dichloro)]-di-s-triazinetriene, and mixtures thereof.

The term "bromide ion donor" means any compound that will generate bromide ions when dissolved in water.

The term "tablet" includes other solid, compressed forms such as sticks and pucks.

SUMMARY OF THE INVENTION

The present invention relates to hypochlorite donor/bromide ion donor tablets for disinfecting recirculating water systems, and more particularly to tablets comprising chlorinated isocyanurates, sodium bromide, and a stabilizer which regulates the rate at which the chlorinated isocyanurate and the sodium bromide

are dissolved or dispersed in flowing water. The tablets according to the invention are stable in water, i.e., the tablets do not disintegrate into fines upon exposure to flowing water, but instead dissolve at relatively uniform and commercially acceptable rates.

In one preferred embodiment of the invention, the tablets are comprised of the following solid particulate materials:

- a) chlorinated isocyanurates; and
- b) sodium bromide; and
- c) a stabilizer selected from active chlorine stabilizer compounds that are compatible, i.e., unreactive, with chlorinated isocyanurates in the solid state, and capable of binding active halogen (chlorine or bromine in the +1 valence state), and less soluble when fully chlorinated than in the less than fully chlorinated state.

In another embodiment of the invention, the tablets are comprised of the following solid particulate materials:

- a) chlorinated isocyanurates; and
- b) sodium bromide encapsulated with a stabilizer selected from coating agents having a low solubility in aqueous media.

The tablets according to the invention are stable in water, i.e., they do not disintegrate into fines upon exposure to flowing water, but instead dissolve at relatively uniform and commercially acceptable rates.

Preferred tablet compositions are those comprising from about 62 wt.% to about 97 wt.% chlorinated isocyanurate, from about 1 wt.% to about 30 wt.% sodium bromide, and from about 2 wt.% to about 8 wt.% stabilizer wherein the stabilizer is an active chlorine stabilizer compound that is compatible with chlorinated

isocyanurates in the solid state, and capable of binding active halogen (chlorine or bromine in the +1 valence state), and less soluble when fully chlorinated than in the less than fully chlorinated state. The preferred
5 chlorinated isocyanurate is trichloro-s-triazinetriene (also called trichloroisocyanuric acid and trichloroisocyanurate, which is produced and sold by Monsanto Co. under the product name ACL 90^R PLUS. ACL^R is a registered trademark of Monsanto Co.).

10 The invention permits production of water stable tablets containing up to about 30% by weight sodium bromide.

Other features and advantages of the invention will become apparent from the following detailed
15 description, which is directed, by way of illustration only, to compositions comprising trichloro-s-triazinetriene and sodium bromide. These compositions are merely exemplary of various embodiments of the invention, and should not be viewed as a limitation on any claimed
20 invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 illustrates trichloro-s-triazinetriene/sodium bromide tablet structures that provide acceptable water stability properties.

25 FIGURES 2 - 4 illustrate trichloro-s-triazinetriene/sodium bromide tablet structures that are not water stable.

FIGURE 5 illustrates an erosion feeder apparatus.

30 DETAILED DESCRIPTION OF THE INVENTION

It has now been discovered that the problem with making water stable tablets from mixtures of chlorinated isocyanurates and sodium bromide is the large difference in the solubilities of the two materials. For
35 example, trichloro-s-triazinetriene has a solubility limit of 1.2 grams per 100 milliliters of water at 25°C, whereas about 105 grams of sodium bromide can be dissolved in the same volume of water. Hence, when tablets comprising these

compounds are immersed in water, the sodium bromide portion will dissolve much faster than the trichloro-s-triazinetriene portion. As a consequence, when mixtures containing more than about 2 wt.% sodium bromide are used, the tablets are unstable in water. The effect of the solubility differences is explained by reference to FIGURES 1 - 4.

The trichloro-s-triazinetriene/sodium bromide tablet structures illustrated in FIGURE 1 exhibit good water stability properties because the highly soluble sodium bromide particles are distributed throughout a continuous matrix of trichloro-s-triazinetriene particles so that the sodium bromide particles are isolated from each other and form a non-continuous matrix. In structure A, the sodium bromide particles are considerably smaller than the trichloro-s-triazinetriene particles and occupy the interstices of the trichloro-s-triazinetriene matrix. In structure B, the sodium bromide and trichloro-s-triazinetriene particles are of similar size and are randomly mixed so that the sodium bromide particles occupy some of the interstices of the trichloro-s-triazinetriene matrix. In both structures A and B, each sodium bromide particle is completely surrounded by trichloro-s-triazinetriene particles so that the sodium bromide cannot form a continuous matrix. Thus, when tablets with these structures are submerged in water, the exposed sodium bromide particles dissolve rapidly, but the integrity of the tablet structure is maintained because the water has to dissolve the less soluble trichloro-s-triazinetriene particles before it dissolves another sodium bromide particle.

However, if conventional tableting processes are used on mixtures of trichloro-s-triazinetriene and sodium bromide particles containing more than about 2 wt.% sodium bromide, the result is often tablets having the composite structures illustrated in FIGURES 2 - 4. These tablets may have a semi-continuous or continuous network of small sodium bromide particles, voids, or microcracks.

Such structures allow water to penetrate the tablet and rapidly dissolve the sodium bromide. As a consequence, these tablets have little structural integrity and crack into pieces or disintegrate into fines upon exposure to water.

It has now been found that the water stability of trichloro-s-triazinetriene/sodium bromide tablets is dramatically improved when certain tablet stabilizers belonging to the class of compounds known to be active chlorine stabilizers are included in the tablet composition. These stabilizers extend the range of water stable trichloro-s-triazinetriene/sodium bromide tablets to mixtures containing up to about 30 wt.% sodium bromide. Tablets containing up to about 30 wt.% sodium bromide are desirable for recirculating water systems contaminated by ammonia.

While not wishing to be bound by theory, it is believed that these advantageous results are obtained because the tablet stabilizers work by the following mechanism, using 5,5-dimethylhydantoin ("DMH") as an example. DMH is quite water soluble, so that it dissolves quickly as water enters the tablet. As the dissolved DMH diffuses toward the surface of the tablet, it is chlorinated by dissolved HOCl that is released by the trichloro-s-triazinetriene. The fully chlorinated DMH, 1,3-dichloro-5,5-dimethylhydantoin, is less soluble in water and precipitates in the pores of the tablet. The precipitate blocks the pores so water cannot wick into the interior of the tablet and sodium bromide cannot dissolve out.

It is contemplated that only a small amount of the tablet stabilizer is needed, just enough to block the pores of the tablet. It is also contemplated that only those active chlorine stabilizers for which the fully chlorinated molecule is considerably less soluble than the non-chlorinated or partially chlorinated derivative will be effective in improving tablet water stability. Finally, the mechanism contemplates that the fully

chlorinated and/or brominated analogs of the additives will be ineffective in improving the water stability of trichloro-s-triazinetriene/sodium bromide tablets.

To be effective, the stabilizer must meet the following criteria:

- 1) the stabilizer must be compatible, i.e., unreactive, with chlorinated isocyanurates in the solid state; and
- 2) the stabilizer must be capable of binding active halogen (chlorine or bromine in the +1 valence state); and
- 3) the stabilizer must be less soluble when fully chlorinated than when less than fully chlorinated.

The water stability tests described in the following TABLES 2 -5 were conducted using a transparent (plexiglass) erosion feeder measuring 6" wide by 18" tall. The erosion feeder is illustrated in FIGURE 5.

The water flow for all of the tests reported was standardized at 1.0 gal/min and the water temperature was 80°F, since the extent of tablet cracking was dependent on both water flow rate and temperature. After the tablets were placed in the feeder, the water flow was started and the tablets were observed for several hours, up to 48 hours.

The trichloro-s-triazinetriene material used in these tests was Monsanto ACL^R 90G and ACL^R 90XG, commercial grades of trichloro-s-triazinetriene that differ only in their particle size distributions.

The sodium bromide material used had the particle size distribution described in Table 1.

TABLE 1

Sieve Analyses of NaBr Materials
Used to Demonstrate Invention

5	Weight Fraction, %		
	<u>Sieves</u>	<u>Product A</u>	<u>Product C</u>
	+10	0.0	0.0
	-10,+12	0.0	0.0
	-12,+16	0.0	Trace
10	-16,+30	16.5	19.84
	-30,+40	43.0	52.34
	-40,+60	38.0	85.07
	-60	2.2	14.93

Tablets were prepared using standard well-known procedures. In each experiment, the proper amounts of the desired components were weighed out to produce a total of 100 grams. The components were then thoroughly mixed by tumbling in a closed jar. Six 15 gram tablets were made from the mixture using a Carver Model C hydraulic press and a 1.125 inch I.D. stainless steel die. The area of the punch face was 1.00 square inches. The maximum applied tableting pressure and the dwell time were set using the controls for the hydraulic drive. The dwell time was held at 2 seconds. Tablets were made at the specified tableting pressures for a given composition.

Tablet water stability was evaluated by visual examination. As the tablets dissolved, they were visually examined for the development of cracks. Tablets were judged to be water stable if the tablets survived for more than eight hours under the standard conditions without cracking through the entire height or width of the tablet, since very minor cracks did not seriously affect the dissolution rate.

The data in TABLE 2 show that the addition of DMH at levels of 2 wt.% makes it possible to increase the NaBr content to 15 wt.% and still obtain water stable tablets. The data also show that the addition of 4 wt.% DMH allows the production of water stable tablets with up to 20 wt.%

NaBr. In addition, the data shows that the addition of 8 wt.% DMH allows the production of water stable tablets with up to 30 wt.% NaBr.

5

TABLE 2

Effect of Adding Dimethylhydantoin on the Water
Stability of ACL® 90/NaBr One-Inch Tablets

	<u>Weight Ratio</u>			<u>Grade of</u>	<u>Tabletting Pressure</u>
	<u>ACL® 90</u>	<u>NaBr*</u>	<u>DMH</u>		
10	85	15	0	G	16 (Tablet Not Stable)
	84.5	15	0.5	G	12 Tablet Stable
	84.5	15	1	G	11 Tablet Stable
15	83	15	2	G	10 Tablet Stable
	81	15	4	G	10 Tablet Stable
<hr/>					
	80	20	0	G	>16 (Tablet Not Stable)
	79	20	1	G	12 Tablet Stable
20	78	20	2	G	10 Tablet Stable
	76	20	4	G	10 Tablet Stable
<hr/>					
	85	15	0	XG	14 (Tablet Not Stable)
	84.5	15	0.5	XG	12 Tablet Stable
25	84	15	1	XG	10 Tablet Stable
	83	15	2	XG	10 Tablet Stable
	81	15	4	XG	12 Tablet Stable
<hr/>					
	70	30	0	G	12 (Tablet Not Stable)
30	62	30	8	G	12 Tablet Stable

*NaBr Product A

The data in TABLE 3 show that glycoluril can be blended with ACL[®] 90/NaBr mixtures to produce water stable tablets with NaBr contents up to 30 wt.%.

TABLE 3

Effect of Adding Glycoluril on the Water Stability of ACL[®] 90/NaBr One-Inch Tablets

	Weight Ratio			Grade of Tabletting Pressure	
	ACL [®] 90	NaBr	Gly.	ACL [®] 90	Required (k psi)
5	85	15	0	G	16 (Tablet Not Stable)
10	81	15	4	G	6 Tablet Stable
15	80	20	0	G	>16 (Tablet Not Stable)
20	76	20	4	G	8 Tablet Stable
25	70	30	0	G	12 (Tablet Not Stable)
30	62	30	8	G	12 Tablet Stable

The data in TABLE 4 show that cyanuric acid does not improve the water stability of ACL[®] 90/NaBr tablets even though it is known to be a chlorine stabilizing agent. As shown in TABLE 5, cyanuric acid is less soluble than either dichloro- or trichloro-isocyanuric acid. Thus, cyanuric acid does not meet the criteria for effective tablet stabilizers.

TABLE 4

Effect of Other Additives on the Water
Stability of ACL^R 90/NaBr One-Inch Tablets

	<u>Weight Ratio</u>			<u>Additive</u>	<u>Grade of</u> <u>ACL^R 90</u>	<u>Tabletting</u> <u>Pressure</u> <u>Required</u> <u>(k psi)</u>
	<u>ACL^R 90</u>	<u>NaBr</u>	<u>Add.</u>			
5						
10	85	15	0	--	G	16 Tablet Not Stable
15	81	15	4	Cyanuric Acid	G	14 Tablet Not Stable
20	81	15	4	Phthalimide	G	16 Tablet Not Stable
	81	15	4	Toluenesulfon -imide	G	>16 Tablet Not Stable
25	81	15	4	Glutarimide	G	8 Tablet Stable
30	62	30	8	Glutarimide	G	12 Tablet Stable

TABLE 5Solubilities of Some Additives and Their
Chlorinated Derivatives

	<u>Compound</u>	<u>Temperature Solubility in Water</u>	
		<u>(°C)</u>	<u>(gm/100 gm Water)</u>
10	Cyanuric acid	25	0.2
	Dichloroisocyanuric acid	25	0.8
	Trichloroisocyanuric acid	25	1.2
	Dimethylhydantoin	20	13.5
	Chloro-dimethylhydantoin	25	0.87
15	Dichloro-dimethylhydantoin	25	0.16
	Glycoluril	17	0.1
	Dichloroglycoluril	20	0.47
	Tetrachloroglycoluril	25	0.008
	p-Toluenesulfonamide	25	0.32
20	N-Chloro-toluenesulfonamide	--	--
	N,N-Dichloro-toluenesulfonamide	--	--
	Phthalimide	25	0.06
	N-Chlorophthalimide	--	--

25

The data in TABLE 4 further show that phthalimide and toluenesulfonimide are not effective in improving the water stability of ACL^R 90/NaBr tablets, but that glutarimide is at least as effective as DMH as a water stability additive.

30

In another embodiment of the invention, it is contemplated that water stable trichloro-s-triazinetriene/sodium bromide tablets containing greater than about 15 wt.% sodium bromide may be obtained by encapsulating the sodium bromide particles with a low-solubility coating.

35

In addition to the tablet components described above, the tablet compositions may optionally contain other ingredients such as fillers, binders, scale inhibitors, corrosion inhibitors, and other components known to one skilled in the art.

40

Use of higher tableting pressures allows harder, denser tablets to be made. At high tableting pressures, use of a mold release agent or lubricant reduces damage to the tablet upon ejection from the tableting die. Any material commonly used to lubricate dies and aid in the tableting of ACL^R 90 may be used, but preferred lubricants are any of the stearate lubricants. However, mixing the stearate lubricant into the bulk of the tablet is not preferred since this may adversely affect the water stability by interfering with the binding between ACL^R 90 particles. Instead, the stearate is preferably applied using a puffer system, which applies the lubricant directly onto the walls of the punches and die. In this way, only the external surface of the tablet is lubricated and the tablet contains a negligible amount of stearate.

Moisture also adversely affects the water stability of tablets. Moisture causes a reaction to occur between the ACL^R 90 and sodium bromide particles. This reaction results in the formation of bromine gas, a noxious, pungent smelling, reddish-brown gas. This gas is a health hazard to personnel operating the blending and tableting units. In addition, it leads to severe corrosion of the equipment. Therefore, it is preferable to use a sodium bromide material with a moisture content below 0.4 wt.% and more preferably below 0.2 wt.%. Use of a dry air purge is also important to insure that the moisture level does not exceed these limits during handling, due to the hygroscopic nature of the sodium bromide.

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

IN THE CLAIMS:

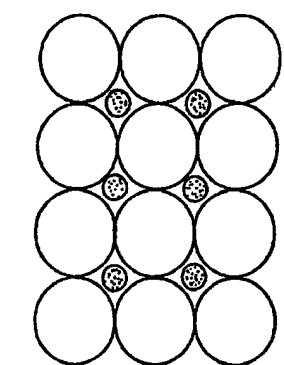
1. A water stable tablet for disinfecting recirculating water systems that provides prolonged and controlled release of hypobromous acid when immersed in water comprising the following solid particulate materials:
- a) chlorinated isocyanurates; and
 - b) sodium bromide having a moisture content less than about 0.4 wt.%; and
 - c) a stabilizer selected from active chlorine stabilizer compounds that are compatible with chlorinated isocyanurates in the solid state, and capable of binding active halogen (chlorine or bromine in the +1 valence state), and less soluble when fully chlorinated than in the less than fully chlorinated state.
2. The tablet of claim 1 wherein the chlorinated isocyanurate is dichloroisocyanuric acid, trichloro-s-triazinetriene, [mono(trichloro)-tetra(monopotassium dichloro)]-penta-s-triazinetriene, [mono(trichloro)-mono(monopotassium dichloro)]-di-s-triazinetriene, or mixtures thereof.
3. The tablet of claim 1 wherein the active chlorine stabilizer compound is 5,5-dimethylhydantoin, glycoluril, or glutarimide.
4. The tablet of claim 1 comprising from about 62 wt.% to about 97 wt.% chlorinated isocyanurate, from about 1 wt.% to about 30 wt.% sodium bromide, and from about 2 wt.% to about 8 wt.% active chlorine stabilizer compound.

5. The tablet of claim 4 comprising trichloro-s-triazinetriene, sodium bromide, and 5,5-dimethylhydantoin.

5 6. A water stable tablet for disinfecting recirculating water systems that provides prolonged and controlled release of hypobromous acid when immersed in water comprising the following solid particulate materials:

- a) chlorinated isocyanurates; and
- 10 b) sodium bromide, wherein the particles have been encapsulated with a coating agent having a low solubility in aqueous media.

1/2



○ ACL 90 GRANULES
 ⊗ NaBr GRANULES

FIG. 1A

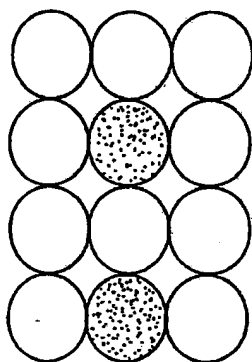


FIG. 1B

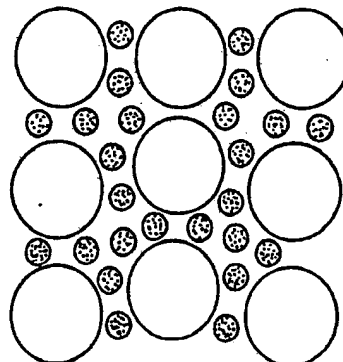


FIG. 2

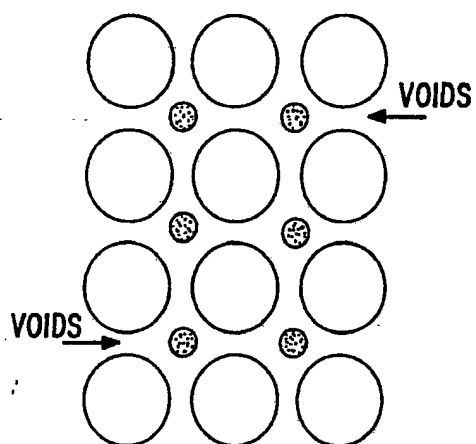


FIG. 3

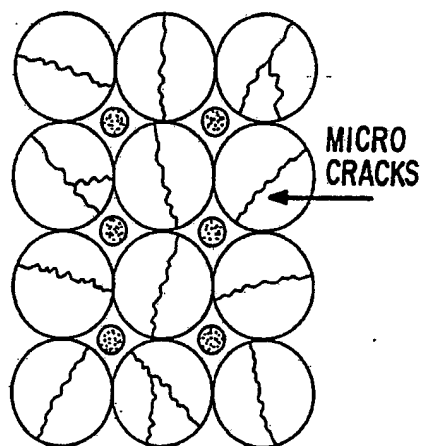


FIG. 4

2/2

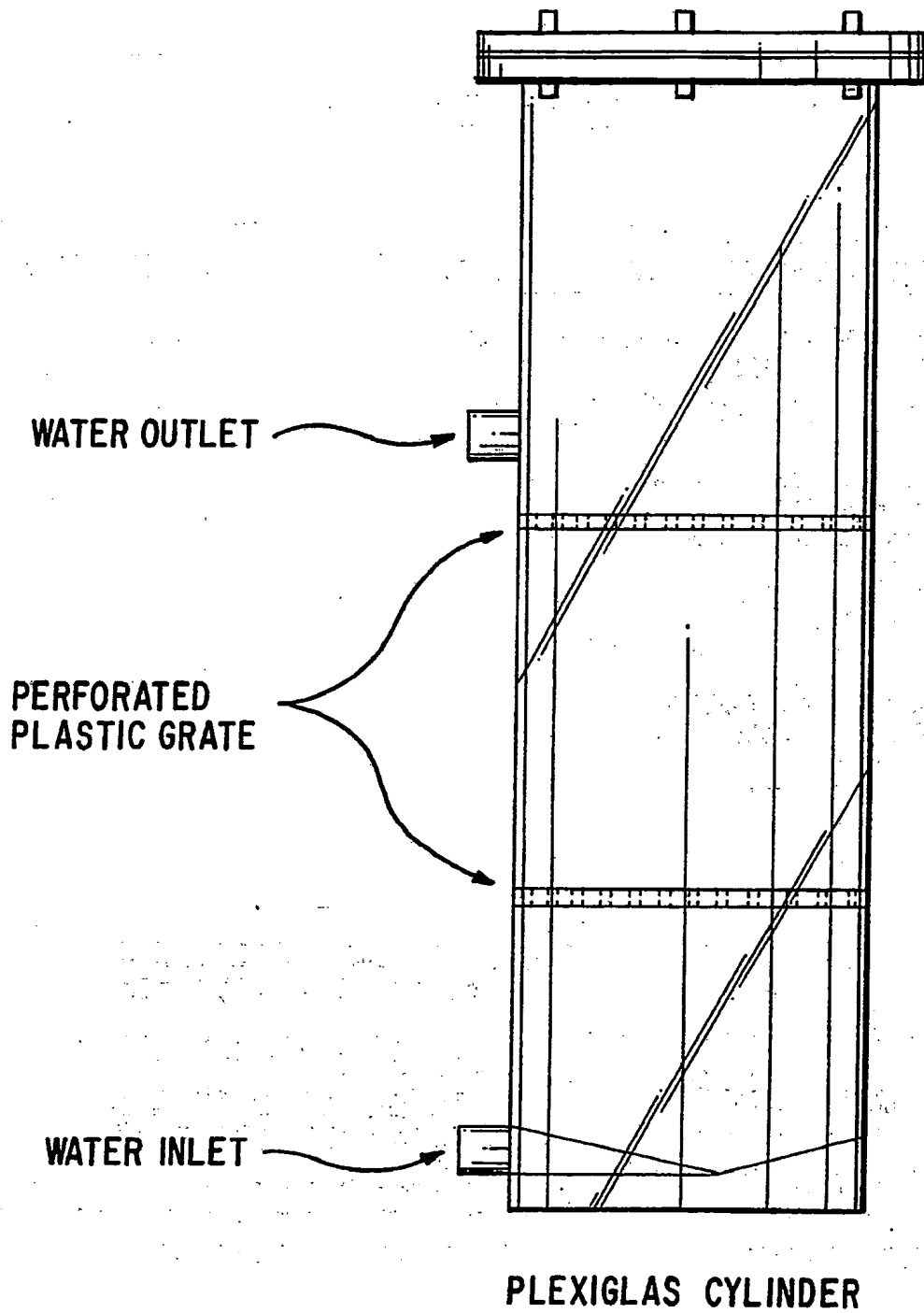


FIG. 5

INTERNATIONAL SEARCH REPORT

PCT/US 92/06735

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C02F1/76; C02F1/50		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C02F ; A01N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 403 465 (THE UNIVERSITY OF HOUSTON) 19 December 1990 see page 9, line 19 - page 10, line 2; claims 12-18,35-38; example 16 ---	1-5
A	US,A,4 698 165 (THEYSON) 6 October 1987 see column 2, line 64 - line 66 ---	1
A	EP,A,0 427 517 (BIO-LAB) 15 May 1991 see claims 1,3-13; example 3 ---	1-5
A	US,A,4 557 926 (NELSON) 10 December 1985 see abstract -----	1
<p>⁹ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
27 OCTOBER 1992		02.11.92
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer KASPERS H.M.C.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9206735
SA 63707**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0403465	19-12-90	AU-A- 5924890	08-01-91
		EP-A- 0429631	05-06-91
		WO-A- 9015780	27-12-90
<hr/>			
US-A-4698165	06-10-87	None	
<hr/>			
EP-A-0427517	15-05-91	US-A- 5015643	14-05-91
		AU-A- 6585890	23-05-91
		JP-A- 3221194	30-09-91
<hr/>			
US-A-4557926	10-12-85	AU-B- 559310	05-03-87
		AU-A- 3274084	14-03-85
		BE-A- 900498	05-03-85
		CA-A- 1230280	15-12-87
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